Composites Part B 109 (2017) 82–90

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Polymer nano-composite films with inorganic upconversion phosphor and electro-optic additives made by concurrent triple-beam matrix assisted and direct pulsed laser deposition

Abdalla M. Darwish [a,*], Shaelynn Moore [a], Aziz Mohammad [a], Deonte' Alexander [a], Tyler Bastian [a], Wydglif Dorlus [a], Sergey Sarkisov [b], Darayas Patel [c], Paolo Mele [d], Brent Koplitz [e], David Hui [f]

[a] Physics Department, Dillard University, New Orleans, LA 70122, USA
[b] SSS Optical Technologies, 515 Sparkman Drive, Huntsville, AL 35816, USA
[c] Oakwood University, Department of Mathematics & Computer Science, 7000 Adventist Blvd, Huntsville, AL 35896, USA
[d] Muroran Institute of Technology College of Design and Manufacturing Technology Research Center for Environmentally Friendly Materials Engineering, 27-1 Mizumoto-cho, Muroran, Hokkaido, 050-8585, Japan
[e] Chemistry Department, Tulane University, New Orleans, LA 70122, USA
[f] Mechanical Engineering Department, University of New Orleans, New Orleans, LA 70148, USA

ARTICLE INFO

Article history:
Received 5 September 2016
Accepted 19 October 2016
Available online 20 October 2016

Keywords:
Nano-composite polymer films
Pulsed laser deposition
Matrix assisted pulsed laser evaporation
Rare earth upconversion phosphors
Multiple beam multiple target pulsed laser deposition

ABSTRACT

The work was to investigate polymer nano-composite films with two inorganic additives: upconversion fluorescent phosphor $NaYF_4:Yb^{3+}$, Er^{3+} and aluminum doped ZnO (AZO). The films were deposited using a new method of concurrent evaporation of the frozen solution of polymer poly(methyl methacrylate) (PMMA) using the matrix assisted pulsed laser evaporation (MAPLE) and the ablation of the phosphor and AZO targets using the pulsed laser deposition (PLD). Three laser beams, an infrared 1064-nm beam for the MAPLE and two 532-nm beams for the PLD targets, were concurrently used in the process. A new target holder with remote control of the target tilt was designed to provide overlapping of the plumes from the three targets and uniform mixing of the additives in the polymer film. The fabricated nano-composite films were characterized using X-ray diffraction, scanning electron microscopy (SEM), and the measurement of the quantum efficiency (QE) of the upconversion fluorescence. The films retained the crystalline structure of the inorganic additives. The size of the nano-particles varied in the range 10–200 nm. Upconversion QE of the films was an order of magnitude less than that of the bulk phosphor, which can be explained by lesser number of the rare-earth ions in the nano-particles in the polymer film than in the micro-grains of the bulk phosphor. The AZO additive increased QE by 1.6 times to (0.072 ± 0.022) % more likely due to the plasmonic enhancement of the local optical infra-red pump (980 nm) field. The proposed triple-beam triple-target MAPLE/PLD method can be potentially used for making a wide variety of nano-composite films.

1. Introduction

There has been an explosive interest in the technique of laser assisted deposition of polymer nano-composite films exploiting the matrix assisted pulsed laser evaporation (MAPLE) with regard to the polymer host as can be judged form the numerous recent publications [1–40]. In MAPLE, a frozen solution of a polymer in a relatively volatile solvent is used as a laser target. The solvent and concentration are selected so that first, the polymer of interest can dissolve to form a dilute, particulate free solution, second, the majority of the laser energy is initially absorbed by the solvent molecules and not by the solute molecules, and third, there is no photochemical reaction between the solvent and the solute. The light-material interaction in MAPLE can be described as a photo-thermal process. The photon energy absorbed by the solvent is converted to thermal energy that causes the polymer to be heated but the solvent to vaporize. As the surface solvent molecules are evaporated into the gas phase, polymer molecules are exposed at

* Corresponding author.
E-mail address: adarwish@bellsouth.net (A.M. Darwish).

http://dx.doi.org/10.1016/j.compositesb.2016.10.053
1359-8368/

the gas-target matrix interface. The polymer molecules attain sufficient kinetic energy through collective collisions with the evaporating solvent molecules, to be transferred into the gas phase. By careful optimization of the MAPLE deposition conditions (laser wavelength, repetition rate, solvent type, concentration, temperature, and background gas and gas pressure), this process can occur without any significant polymer decomposition. The MAPLE process proceeds layer-by-layer, depleting the target of solvent and polymer in the same concentration as the starting matrix. When a substrate is positioned directly in the path of the plume, a coating starts to form from the evaporated polymer molecules, while the volatile solvent molecules are evacuated by the pump from the deposition chamber. In case of fabrication of polymer nano-composites, MAPLE targets are usually prepared as nano-colloids of the additives of interest in the initial polymer solutions.

Mixing the components of different nature, organic polymers and inorganic dopants, in the same target at a certain proportion and exposing them to the same laser beam not necessarily brings good quality nano-composite films. The laser pulse energy and wavelength cannot be optimized for each component individually. Also, the mixing proportion in the composite film is dictated by the initial proportion of the target and thus cannot be changed in the process. These limitations were removed in the recently proposed method of multi-beam and multi-target deposition (in its double-beam/dual-target variation) using a MAPLE polymer target and one inorganic target, each being concurrently exposed to laser beams of different wavelengths [41–50]. Using the method, nano-composite films of polymer poly(methyl methacrylate) known as PMMA doped with a rare earth (RE) inorganic upconversion phosphor compounds were prepared. Also, a nano-composite film of thermoelectric film of inorganic aluminum-doped ZnO known as AZO was impregnated with PMMA nano-fillers with the purpose of improving electrical conductivity and thermoelectric performance [46,50]. The polymer target was a frozen (to a temperature of liquid nitrogen) PMMA solution in chlorobenzene exposed to a 1064-nm laser beam from a Q-switched Nd:YAG pulsed laser. The inorganic targets were the pellets made of the compressed micro-powders of highly efficient RE-doped $NaYF_4$ or the sintered powder of AZO concurrently ablated with the conventional pulsed laser deposition (PLD) process using the 532-nm frequency doubled beam from the same laser. The major result was that both, the polymer and the inorganic components could be transferred on a substrate during the combined MAPLE/PLD process in the form of a uniformly mixed nano-composite film preserving the chemical/crystalline structure of the components and with the desired new functional properties (highly efficient upconversion emission or the improved thermoelectric energy harvesting). The early work was limited to two laser beams and two targets (polymer MAPLE and inorganic PLD). Also, the target tilt (in order to provide overlapping of the plumes from both targets on the substrate) was adjusted manually inside the open vacuum chamber before the deposition process. Any correction of the plume directions in order to optimize the overlapping required time consuming operations of opening the chamber followed by degassing and reaching high vacuum. This paper presents the results of the further improvements of the proposed method. The number of the laser beams and the targets is increased to three: one polymer MAPLE and two inorganic PLD targets. The MAPLE target is the frozen solution of PMMA. The inorganic targets are made of an upconversion phosphor and aluminum doped oxide ZnO known as AZO. The targets are tilted remotely without opening the chamber in such a way that the plum overlapping can be optimized during the deposition process. The focus is on preserving the chemical and crystalline structure of the components in the resulting polymer nano-composite films with two inorganic additives and gaining the functionalities attributed to the additives and their interaction with the polymer host and with each other.

2. Methods and materials

2.1. Triple-beam triple-target MAPLE/PLD system with remotely controlled target tilting

The design of the proposed triple-beam triple-target deposition system (for the sake of simplicity presented for two beams and two targets) is shown in Fig. 1. Remotely controlled vacuum compatible linear actuators tilt the targets in order to achieve an optimal angle θ between the plumes (which are perpendicular to the target surfaces) at which the plumes overlap on the surface of the substrate. This secures the uniform mixing of the materials form the targets in the composite film during the deposition process. The images of the tilt control sub-system for three targets are presented in Figs. 2 and 3. One important advantage of this sub-system as compared to the previous double-beam PLD system [41–50] is that the target holders are tilted around the axes in the horizontal plane instead of vertical plane, which prevents from dropping or spilling the target material.

One of the target holders of the above-mentioned triple-target sub-system is designed to accommodate a MAPLE target cooled with flowing liquid nitrogen (LN) as presented in Figs. 4 and 5. A copper container (cup) for a polymer solution is mounted on a copper container for LN (the cooler) that will be cooling the polymer solution (the target) and keeping it frozen. The MAPLE target assembly is connected to the LN feeding and collecting lines (copper tubing) drawn through a flange to be attached to the vacuum chamber. The feeding line is connected to the LN feeding vessel external to the vacuum chamber. The collecting LN line is

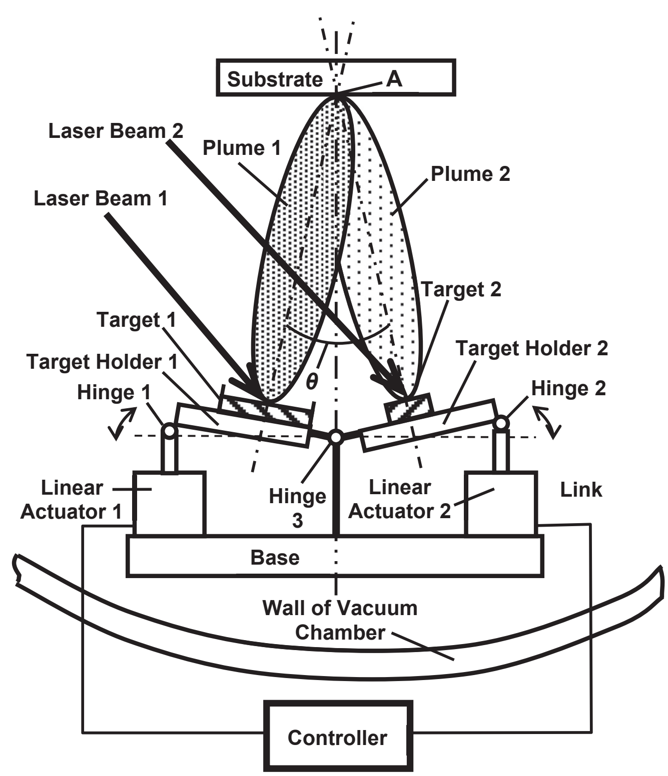

Fig. 1. Schematic of the target tilting sub-system of the new multi-beam multi-target PLD/MAPLE system with remote control of the directions of the plumes. Shown are two targets out of three. Θ is the optimal angle between the plums when they overlap in point *A* on the surface of the substrate.